

Polyurethanes with Monodisperse Rigid Segments Based on a Diamine–Diamide Chain Extender

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ABSTRACT: Polyether(bisurethane-bisurea-bisamide)s (PEUUA) based on poly(tetramethylene oxide) (PTMO) were synthesized by chain extension of PTMO endcapped with a diisocyanate (DI), and a diamine–diamide extender. The prepolymers were PTMOs with molecular weights between 1270 and 2200 g mol⁻¹, either endcapped with 4,4'-diphenylmethane diisocyanate (MDI), 2,4-toluene diisocyanate (2,4-TDI), or 1,6-hexane diisocyanate (HDI) and with a low content of free diisocyanate (<0.1 wt %). The diamine–diamide (6A6) extender was based on hexamethylene diamine (6) and adipic acid (A). In this way, segmented polyurethanes with monodisperse rigid segments (DI-6A6-DI) were obtained. The PEUUAs were characterized by DSC as well as temperature-dependent FTIR and DMTA. The mechanical properties of the polymers were evaluated by compression set and tensile test measurements. The polyurethanes with monodisperse rigid segments displayed low glass transition

temperatures, almost temperature-independent rubbery plateaus and sharp melting temperatures. The crystallinities of the hard segments were 70–80% upon heating and 40–60% upon cooling. The rate of crystallization was moderately fast as the supercooling ($T_m - T_c$) was in the order 36–54°C. The polyurethanes based on HDI had a much higher rubber modulus as compared to the MDI and 2,4-TDI-based polymers, because of a higher degree of crystallinity and/or a higher aspect ratio of the crystallites. The HDI residues are flexible and not sterically hindered and could therefore be more easily packed than MDI or 2,4-TDI residues. Polyurethanes with monodisperse DI-6A6-DI hard segments have interesting properties. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2180–2189, 2008

Key words: polyurethane; monodisperse; amide; properties; segmented block copolymer

INTRODUCTION

Polyurethane elastomers consist of alternating segments of flexible polyether and rigid urethane or urea, and are classified as thermoplastic polyurethanes (TPUs).^{1,2} Because of the incompatibility of the alternating segments, microphase separation easily occurs. The rigid segments phase separates into hard domains dispersed in a soft matrix, and these hard phases simultaneously act as thermo reversible physical crosslinks that allow melt processing and as reinforcing fillers that increase the modulus. Phase separation either occurs by liquid–liquid demixing and/or (partial) crystallization of the rigid segments. Liquid–liquid demixing in segmented block copolymers leads to an aggregation of the rigid segments, resulting in spherical hard domains that hardly contribute to the reinforcement of the polymer matrix.³ Liquid–liquid demixing is favored by the presence of long rigid

segments and can be avoided if one employs short uniform rigid segments. Most commercial TPUs have a random distribution of the rigid segments, resulting in a complex morphology and a low degree of crystallinity; normally lower than 20%.⁴ When the rigid segments are dissolved in a polyether phase, the T_g of the soft phase is increased and broadened, resulting in a poorer flexibility at low temperature. The modulus of segmented block copolymers at room temperature depends on the content and the morphology of the phase-separated rigid segments.^{3,5} If phase separation is merely a result of crystallization, the modulus increases significantly with the content of rigid segments.^{5,6}

Monodisperse crystallizable segments can be used to induce phase separation by crystallization.^{3,5–15} Polyurethanes with monodisperse crystallizable rigid segments have a low T_g of the polyether phase, a relatively high modulus at room temperature, an almost temperature-independent rubber modulus, and a sharp melting transition.^{7–12} However, the mechanical properties of polyurethanes containing monodisperse rigid segments deteriorate when the dispersity of these segments is increased, for instance, by transurethanization or when degradation takes place. These phenomena can occur above 180–210°C.^{9,12,16} It is

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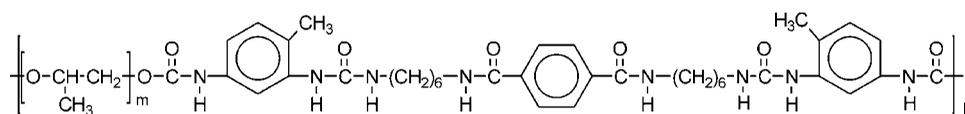


Figure 1 The chemical structure of a PPO-based polyether(bisurethane-bisurea-bisamide) (PPO-TDI-6T6-TDI) with monodisperse rigid segments (TDI-6T6-TDI) as used in a previous study.

therefore difficult to prepare high-melting polyurethanes with monodisperse rigid segments by melt polymerization. Also, these polymers can lose their uniformity upon melt processing.⁹

The dispersity of the rigid segments depends on the polymerization procedure. A prepolymer endcapped with a diisocyanate is reacted with an extender. For mono disperse hard segments, the prepolymer should not contain free diisocyanates, the extender should be uniform in length, and the polymerization temperature should be kept low. Free diisocyanates in the prepolymer can react with an extender and form longer blocks. Another reason for using prepolymers with low contents of free diisocyanate is their lower toxicity.

Several studies have reported on polyurethanes with uniform extenders.^{7–12} Polyurethanes with monodisperse rigid segments have higher moduli, higher yield stresses, higher strengths, and toughness compared with analogous polymers with poly disperse rigid segments. Also, diamine–diamides have been used as monodisperse extenders and the resulting copolymers were poly(ether-urethane-urea-amide)s (PEUUA).¹² In the present study, poly(propylene oxide) endcapped with 2,4-toluene diisocyanate (2,4-TDI) and the uniform diamine–amide extender 6T6-diamine diamide has been used in a previous study. The chemical structure of the resulting PEUUA can be seen in Figure 1.

The TPUs with monodisperse TDI-6T6-TDI segments had rubbery plateaus that were more or less temperature-independent. They also had a well-defined melting temperature (169°C) and interesting elastic properties. These polyurethanes extended with amide were more thermally stable than normal polyurethanes. However, the storage modulus at 25°C of PPO₂₃₀₀-TDI-6T6-TDI was only 13 MPa. This is appreciably lesser than the storage modulus of 28 MPa for an analogous poly(etherester amide), PPO₂₃₀₀-T6T6T, with an equivalent content of rigid segment.¹⁵ This suggests that PEUUA copolymers with hard TDI-6T6-TDI segments had either a degree of crystallinity and/or aspect ratio of the crystallites that was lower than for the corresponding poly(etherester amide) copolymers. The sterical hindrance of the 2,4-TDI may well have been the reason for this lower crystallinity. It is expected that the type of DI used in these TPUs will have an effect on the crystallinity of the hard segment and thereby on the PU properties.

In the present study, investigations have been carried out on polyether(bisurethane-bisurea-bisamide)s

with monodisperse rigid segments using diisocyanate endcapped PTMOs (DI-PTMO-DI) and a uniform diamine–diamide chain extender (6A6). This chain extender is based on hexamethylene diamine (6) and adipic acid (A). DI-PTMO-DIs with a molecular weight of the PTMO between 1270 and 2200 g mol⁻¹ and with a low content of free diisocyanate (<0.1 wt %) were used. Three diisocyanates were applied as endcappers for the PTMO: 4,4'-diphenylmethane diisocyanate (MDI), 2,4-toluene diisocyanate (2,4-TDI), or 1,6-hexane diisocyanate (HDI). The crystallization behavior of the resulting polymers was studied using differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). The thermo-mechanical behavior of the materials was evaluated with dynamic mechanical thermal analysis (DMTA), their elastic behavior with compression set (CS) measurements, and the stress–strain behavior by tensile testing. The properties of these polyurethanes were compared to poly(etheresteramides) with similar structures.

EXPERIMENTAL

Materials

1,6-Diaminohexane, dimethyl adipate, *N,N*-dimethylacetamide (anhydrous), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), and a 0.5M sodium methoxide solution in methanol were purchased from Aldrich Mijdrecht, The Netherlands and used as received. Poly(tetramethylene oxide) endcapped with diisocyanates, i.e., [HDI-PTMO-HDI ($M_w = 2000$ g mol⁻¹, noncommercial sample) and ($M_w = 1270$ g mol⁻¹, LFH520), 2,4-TDI-PTMO-2,4-TDI ($M_w = 1890$ g mol⁻¹, LF900A), and MDI-PTMO-MDI ($M_w = 2210$ g mol⁻¹, LFM300)] were donated by Crompton Corporation, Middlebury, CT. All prepolymers had low contents of free diisocyanate content (<0.1 wt %). The prepolymers were dried overnight *in vacuo* at 80°C before use. The synthesis of the chain extender 6A6 has been described in detail elsewhere.⁶

Copolymerization

The polymerization of (-PTMO₂₀₀₀-HDI-6A6-HDI-) is given here as an example. A dried 250-mL stainless steel reactor with a nitrogen inlet and magnetic coupling stirrer was charged with HDI-PTMO₂₀₀₀-HDI (30 g, 0.0128 mol) and a solution of 6A6-diamine

(4.39 g, 0.0128 mol) in 100-mL anhydrous *N,N*-dimethylacetamide (DMAc). The stirred reaction mixture was heated to 140°C and was allowed to react for 4 h under nitrogen flow. Subsequently, the pressure was carefully reduced ($P < 20$ mbar) to distill the DMAc from the reaction mixture and then further reduced ($P < 0.3$ mbar) for 60 min. The reactor was then slowly cooled, maintaining low pressure. The obtained copolymer was transparent, colorless and tough.

Compression molding

Test samples for DMTA, CS measurements and tensile testing were compression molded with a 40-ton Lauffer 40 press. TPU (2.1 g) cut into small pieces and dried overnight was spread into a bar-shaped mold (80 mm × 9 mm × 2 mm) and placed between press plates. The temperature of the press was set 20° above the melting temperature of the material without surpassing 230°C. First, air was removed from the polymer in the mold by quickly pressurizing and depressurizing the sample. This procedure was repeated three times before pressing the samples at 10 MP (≈ 8.5 MPa) for 2 min. Subsequently, the press was cooled and the test bars were removed from the mold.

Viscometry

The solution viscosities were measured at a concentration of 0.1 g/dL in a mixture of phenol/1,1,2,2-tetrachloroethane (1 : 1M ratio) at 25°C using a capillary Ubbelohde type 1B, and from these the inherent viscosities were calculated.

Infrared analyses

Infrared transmission spectra were recorded using a Nicolet 20SXB FTIR spectrometer, Cambridge, MA with a resolution of 4 cm⁻¹. Solution cast polymer films (0.05 g/mL in HFIP) of <10 μm thickness were used for temperature-dependent IR recorded at temperatures between room temperature and 210°C. The film was placed in between two pressed KBr pellets under a helium flow. The degree of crystallinity of the rigid segments in the polymers was estimated with the following equation:

$$X_c \text{ FTIR} = \frac{\text{Crystalline amide peak}}{\text{Amorphous} + \text{Crystalline amide peak}} = \frac{\lambda_{25^\circ\text{C}(1630 \text{ cm}^{-1})}}{a \times \lambda_{25^\circ\text{C}(1670 \text{ cm}^{-1})} + \lambda_{25^\circ\text{C}(1630 \text{ cm}^{-1})} \quad (1)$$

where λ_T is the height of the absorption band at temperature T (°C).

The height of the amorphous and crystalline amide peak are related by the factor a , which can be calculated according to the following equation:

$$a = \frac{\text{decrease of crystalline peak (25°C - melt)}}{\text{increase of amorphous peak (25°C - melt)}} = \frac{\lambda_{25^\circ\text{C}(1630 \text{ cm}^{-1})} - \lambda_{\text{melt}(1630 \text{ cm}^{-1})}}{\lambda_{\text{melt}(1670 \text{ cm}^{-1})} - \lambda_{25^\circ\text{C}(1670 \text{ cm}^{-1})} \quad (2)$$

The generated values for a were as follows: MDI, 2.55; HDI2000, 2.78, and TDI, 2.80.

Differential scanning calorimetry

DSC spectra were recorded on a Perkin-Elmer DSC apparatus, Monza, Italy equipped with a PE7700 computer and TAS-7 software. Dried samples of 5–10 mg were heated to $\sim 30^\circ\text{C}$ above the melting temperature and subsequently cooled. Both the heating and cooling rates were 20°C/min. The second heating scan was used to determine the melting peak and enthalpy of the sample. The melting temperature was determined as the maximum peak value. From the cooling curve, the onset of crystallization was taken as the crystallization temperature.

Dynamic mechanical thermal analysis

The compression molded test samples (70 mm × 9 mm × 2 mm) were dried *in vacuo* at 50°C for 24 h before use. DMTA spectra were recorded with a Myrenne ATM3 torsion pendulum, Aachen, Germany at a frequency of 1 Hz and a strain of 0.1%. The storage modulus G' and the loss modulus G'' were measured as functions of temperature. The samples were cooled to -100°C and subsequently heated at a rate of 1°C/min. The glass transition was determined as the peak of the loss modulus, and the flow temperature (T_{flow}) was defined as the temperature where the storage modulus reached 1 MPa. The start of the rubbery plateau, i.e., the intercept of the tangents, is called the flex temperature (T_{flex}). The decrease in storage modulus of the rubbery plateau with increasing temperature is quantified by $\Delta G'$, the % change/°C, which can be calculated according to eq. (3):

$$\Delta G' = \frac{G'_{25^\circ\text{C}} - G'_{(T_{\text{flow}} - 50^\circ\text{C})}}{G'_{T_{\text{flow}} - 50^\circ\text{C}}} \times \frac{1}{\Delta T} \quad (3)$$

ΔT is described as the temperature range: ($T_{\text{flow}} - 50^\circ\text{C}$) – 25°C.

Compression set measurements

Samples for compression set measurements were cut from the compression-molded bars. The measure-

ments were carried out at room temperature according to ASTM 395 B standard. After 24 h, the compression was removed and following half an hour's relaxation, the thickness of the sample was measured. The compression set was taken as the average of four measurements and is defined as follows:

$$\text{Compression set} = \frac{d_0 - d_2}{d_0 - d_1} \times 100\% \quad (\%) \quad (4)$$

where d_0 = thickness before compression (mm); d_1 = thickness during compression (mm); d_2 = thickness after 0.5 h relaxation (mm).

Tensile testing

Stress-strain curves were obtained by performing tensile test measurements on the 2.2-mm thick, compression molded bars, cut into dumbbells (ISO 37 type 2). A Zwick Z020 universal tensile machine, Ulm, Germany equipped with a 500 N load cell was used. The strain was measured with extensometers. The tensile tests were performed in threefold according to ISO 37 at a strain rate of 0.4 s^{-1} (corresponding to a test speed of 60 mm/min).

RESULTS AND DISCUSSION

Polyether(bisurethane-bisurea-bisamide)s with monodisperse rigid segments were synthesized from prepolymers based on poly(tetramethylene oxide) (PTMO) endcapped with various diisocyanates (DI) and a uniform diamine-diamide extender. The three diisocyanates used in this series were 2,4-toluene diisocyanate (2,4-TDI), diphenylmethane diisocyanate (MDI), and 1,6-hexane diisocyanate (HDI) (Fig. 2). The uniform aliphatic chain extender, 6A6-diamine-diamide, was prepared from hexamethylene diamine (6) and adipic acid (A) (Fig. 3).⁶ When synthesizing TPUs with monodisperse rigid segments the uniformity of the extender is important as well as having a low content of free diisocyanates in the endcapped prepolymer. Free diisocyanates can form double blocks (DI-6A6-DI-6A6-DI), resulting in the loss of the monodisperse character of the rigid segments in the copolymer. The prepolymers in this study had a very low content of free diisocyanates (<0.1%), and therefore the formation of double blocks was limited and monodisperse rigid segments were formed. The molecular weights of the PTMO segments in the prepolymer were between 1270 and 2200 g mol^{-1} and are given in Table I.

Synthesis of PEUUA copolymers

The prepolymer, extender, and polymerization setup were dried overnight at 80°C *in vacuo* to remove traces

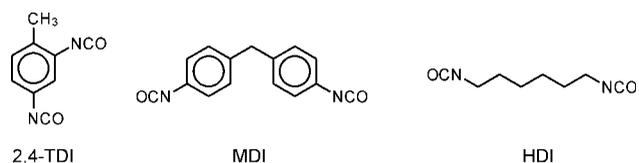


Figure 2 The chemical structures of three diisocyanates; 2,4-TDI, MDI and HDI.

of water. The reaction between the isocyanate end-capped polyether (DI-PTMO-DI) and the diamine-diamide (6A6) was fast, and the polymerization was carried out at a relatively low temperature (140°C). Nevertheless, the components were allowed to react for 4 h to ensure completion. The resulting polymers were nonsticky and transparent materials with inherent viscosities of 1.3–1.6 dL/g (Table II) indicating that the copolymers had high molecular weights in the range commonly obtained. The segmented polyurethanes with HDI were colorless, while the copolymers with MDI and 2,4-TDI were slightly yellowish. This is logical, since polymers based on aliphatic diisocyanates are known to be less colored than their aromatic counterparts.^{1,2}

IR

Infrared spectroscopy was used to study the crystallinity in the PEUUA systems. The absorption bands of carbonyl and N–H groups depend on hydrogen bond formation. Three groups that form hydrogen bonds were present in the systems; urethane, urea and amide groups. Figure 4 gives the absorption bands of polyurethanes in their crystalline and amorphous states, as reported in literature.^{2,11,12,17–19} Urea groups can also form either bidentate or monodentate hydrogen bonds.

The IR spectra of the segmented polyurethanes are displayed in Figure 5. Peaks were observed at 3290 cm^{-1} for the crystalline N–H groups, at 1730 cm^{-1} for the carbonyl group in amorphous urethane, at 1707 cm^{-1} for the carbonyl groups in crystalline urethane, at 1680 cm^{-1} for the monodentate groups in crystalline urea and at 1633 cm^{-1} for the carbonyl groups in crystalline amide (Amide I). The peak at 1599 cm^{-1} was related to the benzene ring and was only observed for the polyurethanes based on MDI and 2,4-TDI. The peaks at 1573, 1538, and 1512 cm^{-1} corresponded to $\delta(\text{N–H}) + \nu(\text{C–N})$ (Amide II).

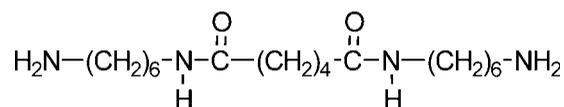


Figure 3 The chemical structure of 6A6 diamine-diamide, used in this study.

TABLE I
Physical Properties for the Polyurethanes with 6A6-diamine–diamide Units

	PTMO (g mol ⁻¹)	DI-PTMO-DI ^a (g mol ⁻¹)	Polymer		Rigid segment				
			RS ^b (%)	η_{inh} (dL/g)	T_m (°C)	T_c (°C)	$T_m - T_c$ (°C)	ΔH_m (J/g)	ΔH_m (J/g RS)
PTMO ₁₈₈₆ -TDI-6A6-TDI	1886	2234	26.8	1.4	151	–	–	9 ^c	–
PTMO ₂₂₀₉ -MDI-6A6-MDI	2209	2710	27.6	1.3	211	176	36	7	25
PTMO ₂₀₀₀ -HDI-6A6-HDI	2000	2336	25.3	1.6	234	181	54	9	36
PTMO ₁₂₇₀ -HDI-6A6-HDI	1270	1606	34.8	1.4	231	176	53	16	46

^a Molecular weights calculated from the NCO concentrations as determined by Crompton Corporation.

^b RS = Rigid segment based on DI-6A6-DI segment, so including the MDI, TDI, or HDI residues.

^c From first heating run.

Although the three segmented polyurethanes had practically the same composition, the IR spectra of the carbonyl groups showed variations in their absorption bands. The IR spectra of the polyurethanes based on TDI and MDI showed strong peaks at 1633 cm⁻¹, representing the carbonyl groups of the crystalline amide. The presence of a small peak at 1707/1696 cm⁻¹ (next to the peak for the amide groups) suggested that some urethane groups were crystalline. However, amorphous urethane groups were also present, as indicated by the peak at 1730 cm⁻¹. No IR peaks corresponding to the urea groups were observed. The IR spectrum of the polyurethane based on HDI showed a strong peak for the crystalline amide units at 1633 cm⁻¹ and for the monodentate bonded crystalline urea at 1680 cm⁻¹. The peak at 1730 cm⁻¹ indicated the presence of some amorphous urea or urethane groups. No peaks were observed for crystalline urethane groups.

Temperature-dependent IR spectroscopy was employed to study the crystallinity of the amide segments as a function of temperature (Fig. 6). The MDI and 2,4-TDI-based polyurethanes displayed equivalent peak changes in their respective IR spectra and therefore only the spectrum for the MDI-based polyurethanes is shown [Fig. 6(a)]. The amide I peaks for the crystalline phase (1630 cm⁻¹) were strong up to the melting temperature of the copolymer. Upon melting, the intensity of this peak decreased, and at the same time the intensity of the peak at 1670 cm⁻¹ of

amorphous C=O groups was found to increase. The absorption bands for the carbonyl group of the crystalline urethane at 1707 cm⁻¹ also decreased in intensity with increasing temperature. Upon cooling of the molten samples, the peaks corresponding to the crystalline carbonyl amide (1630 cm⁻¹) and the crystalline carbonyl urethane (1707 cm⁻¹) only partially recovered.

The HDI-based polyurethane showed a similar decrease in the intensity of the peak at 1633 cm⁻¹ corresponding to the crystalline amide carbonyl and a simultaneous increase in the height of the peak at 1670 cm⁻¹ representing the amorphous amide carbonyl groups [Fig. 6(b)]. Upon heating, the peak of the monodentate crystalline urea groups at 1680 cm⁻¹ also decreased with increasing temperature, while the peak at 1730 cm⁻¹ increased [Fig. 6(b)]. Upon cooling of the sample, the peaks at 1633 and 1680 cm⁻¹ almost completely returned to their initial intensities. This indicates that crystallization of HDI-based rigid segments was easier than crystallization of MDI- and 2,4-TDI-based rigid segments.

The ratio of crystalline and amorphous amide peaks can be used for the determination of the degree of crystallinity for the 6A6 unit in the polymer. The degree of crystallinity for the 6A6 unit in PTMO-MDI-6A6-MDI and PTMO-TDI-6A6-TDI was 70% at room temperature and remained high until the melting temperature [Fig. 7(a)]. Just before the melting tempera-

TABLE II
Thermal and Mechanical Properties of Polyurethanes (DI-6A6-DI) and Poly(etheresteramides) (T6A6T)

Polymer	RS ^a (%)	η_{inh} (dL/g)	T_g (°C)	T_{flex} (°C)	$G'_{25^\circ C}$ (MPa)	T_{flow} (°C)	$\Delta G'$ (%/°C)	E (MPa)	σ_y (MPa)	ε_y (%)	CS (%)
PTMO ₁₈₈₆ -TDI-6A6-TDI	26.8	1.4	-72	5	16	165	0.41	45	6	52	12
PTMO ₂₂₀₉ -MDI-6A6-MDI	27.6	1.3	-63	15	16	205	0.18	45	5	36	18
PTMO ₂₀₀₀ -HDI-6A6-HDI	25.3	1.6	-65	15	32	225	0.88	73	7	43	18
PTMO ₁₂₇₀ -HDI-6A6-HDI	34.8	1.4	-67	-15	50	230	1.02	140	11	30	25
PTMO ₂₀₀₀ -T6A6T ^b	24.1	2.5	-70	10	20	180	0.79	46	9	49	9
PTMO ₁₀₀₀ -T6A6T ^b	38.9	2.9	-60	-15	51	185	0.54	133	12	29	14

^a RS = Rigid segment including urethane or ester groups.

^b Data from Ref. 6 but recalculated with eq. (3).

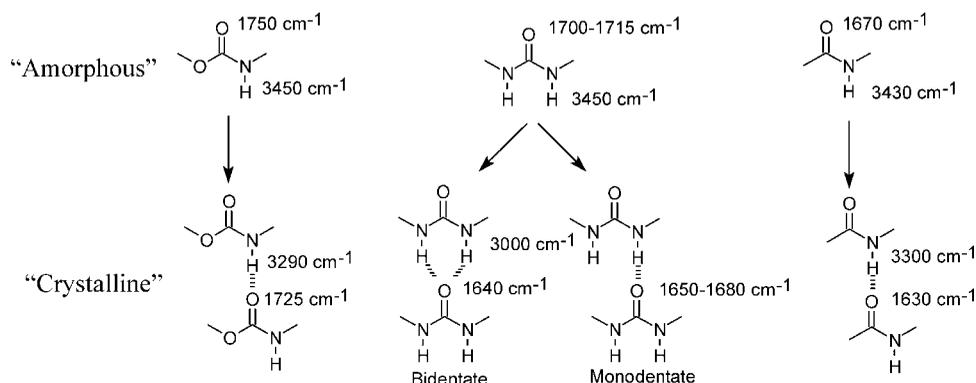


Figure 4 IR absorption bands for urethane, urea and amide groups in their amorphous and crystalline state.

ture, a sharp decrease in crystallinity was observed and upon cooling from the melt, the degree of crystallinity of the 6A6 segments only returned to 40%. The crystallization was thus incomplete and slow, which was probably due to sterical hindrance of the isocyanate residues in the rigid segment.

The degree of crystallinity of the amide units as a function of temperature for the HDI-based polyurethane started at 80%, remained unchanged up to 130°C, decreased sharply at 160°C and approached zero at 180°C [Fig. 7(b)]. Upon cooling, the degree of crystallinity of the amide units increased as the temperature was decreased, eventually reaching 60%. The crystallinity of the 6A6 units in the rigid segments based on HDI was higher than the crystallinity of the corresponding units in rigid segments based on MDI and TDI. Moreover, after melting and subsequent cooling the crystallinity of the 6A6 units in the HDI based rigid segments at room temperature were found to recover to a higher degree than for the 6A6 units in the MDI- and TDI-based rigid segments.

Normally, the absorption bands of the crystalline amide carbonyl groups at 1633 cm^{-1} have a tendency

to decrease just before the melting temperature, as was observed in the case of the MDI- and TDI-based polyurethanes [Fig. 7(a)]. A similar behavior has been observed for PEEAs.⁶ However, for the polyurethane based on HDI-6A6-HDI a sharp decrease of the absorption band representing the carbonyl groups in the crystalline amide was observed at 180°C. This temperature is lower than the melting temperature determined with DSC (i.e., 232°C) or DMTA (i.e., 225°C). The reason for this is as of now unclear.

Rigid segment packing

Sterical hindrance of the DII might affect the crystallization of the urethane segment. The hydrogen bonding possibilities of the extended rigid segments TDI-6A6-TDI and HDI-6A6-HDI are given in Figure 8. Here, the 6A6 units are ideally hydrogen bonded.

In the 2D structures (Fig. 8), the urea groups were monodentate bonded, which was in agreement with the FTIR results. Obviously, the packing of the 2,4-TDI was sterically hindered by the methyl group (Fig. 8). The methyl groups were expected to be in the 4-position with respect to the isocyanate groups that had reacted with the PTMO, as a result of the reactivity of the C_4 -positioned isocyanate group being much higher than the C_2 -positioned one.^{20,21} The methyl groups clearly hindered hydrogen bonding of the urea. The 2,4-TDI group might have turned out of plane to allow bonding of the urea hydrogens, but that would probably also have lowered the hydrogen bonding effect of the urethane. This packing difficulty of the 2,4-TDI (and MDI) groups caused a decrease in the degree of crystallinity of the rigid segments and possibly also in the aspect ratio of the crystallites. The aliphatic HDI had a regular hexamethylene unit that did not sterically hinder the urea from hydrogen bonding (Fig. 8). As a result, the crystallinity of the amide units was higher, and the urea groups of the HDI were allowed to participate in the crystallization. However, according to this 2D structure of the fully

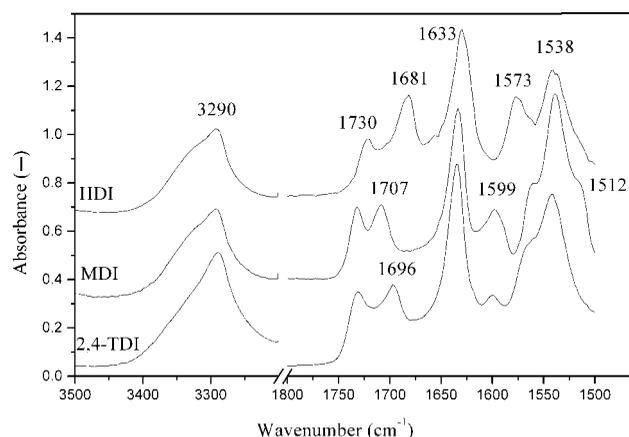


Figure 5 IR spectra of PEUUA: ■, PTMO₂₀₀₀-HDI-6A6-HDI; ▲, PTMO₂₂₀₉-MDI-6A6-MDI; ●, PTMO₁₈₈₆-TDI-6A6-TDI.

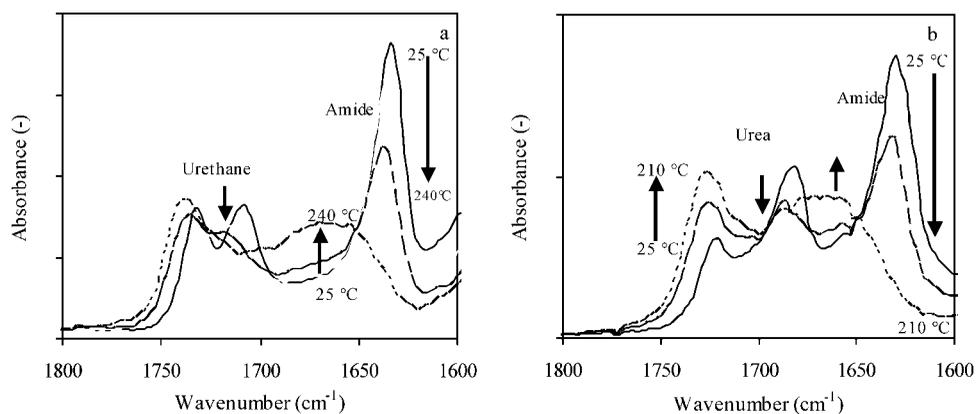


Figure 6 Temperature dependent IR spectra at increasing temperatures of a) PTMO₂₂₀₉-MDI-6A6-MDI ($T_m = 212^\circ\text{C}$); 25, 180, 240°C; and b) PTMO₂₀₀₀-HDI-6A6-HDI ($T_m = 231^\circ\text{C}$); 25, 160, 210°C.

extended chain the H-bonding of the urethane groups was still impossible.

DSC

The melting and crystallization behavior of the segmented polyurethanes was evaluated by DSC. Three endothermic transitions were observed for the polymers. The first transition was due to the crystalline PTMO phase (Table I). The length of the PTMO segment differed slightly for the prepolymers, and increasing the length of this PTMO segment resulted in an increase in melting enthalpy and melting temperature. The second transition was related to a change in the crystalline structure of the amide phase, as is often observed for polyamides.^{14,22,23} This is the transition from triclinic to a pseudo hexagonal packing. During this transition, the distance in the nonhydrogen-bonded direction is changed. This transition was not observed with FTIR, probably as the distance in the H-bonding direction was not changed.

The third transition was due to melting of the rigid segments. The MDI- and HDI-based polyurethanes displayed high melting temperatures of 212 and

231°C, respectively, whereas the 2,4-TDI-based polymer had a lower melting temperature, i.e., 155°C. For the 2,4-TDI-based polyurethane, no crystallization peak or second melting of the hard phase was observed, indicating that the crystallization was slow and the crystallinity low. Therefore, only the melting temperature and enthalpy of the first heating run for the 2,4-TDI-based polyurethane are given in Table I. For the MDI- and HDI-based polyurethanes, on the other hand, both crystallization and melting transition in the second heating run were observed. The HDI copolymers had higher melting temperatures than the copolymers based on MDI, despite the aliphatic nature of HDI. The HDI polyurethanes also had a higher melting enthalpy than the MDI-based ones, and thus the degree of crystallinity for the HDI-based polyurethanes was higher. The supercooling ($T_m - T_c$) was in the range 35–55°C, indicating a relatively fast crystallization of these monodisperse polyurethane segments. However, it was not as fast as for monodisperse rigid segments in PEEA⁶ (Fig. 9).

DMTA

The thermomechanical properties of the polymers were determined by means of DMTA (Fig. 10). It should be noted that the polyurethanes were thermally unstable above 180°C and that the DMTA results may be influenced by their possible degradation. However, the amide-extended TPU was found to be more thermally stable than normal TPUs.¹² The storage and loss modulus of PEUAs based on different isocyanate endcappers are plotted as a function of temperature.

The T_g of the polymers was remarkably low, suggesting a good phase separation (Table II). PTMO segments with a length of 2000 g mol⁻¹ have the ability to crystallize^{6,13,14} and this crystalline polyether phase melts at $\sim 0^\circ\text{C}$, giving a shoulder after the T_g and increasing the T_{flex} to 5–10°C. The rubber modulus was almost temperature independent, the $\Delta G'$ values

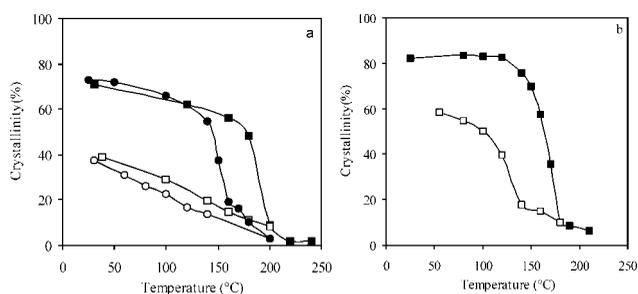


Figure 7 The crystallinity of the amide units in the rigid segments of the polyurethanes as a function of temperature a) ■, □, PTMO₂₂₀₉-MDI-6A6-MDI; ●, ○, PTMO₁₈₈₆-TDI-6A6-TDI; b) PTMO₂₀₀₀-HDI-6A6-HDI: closed symbols, heating curve; open symbols, cooling curve.

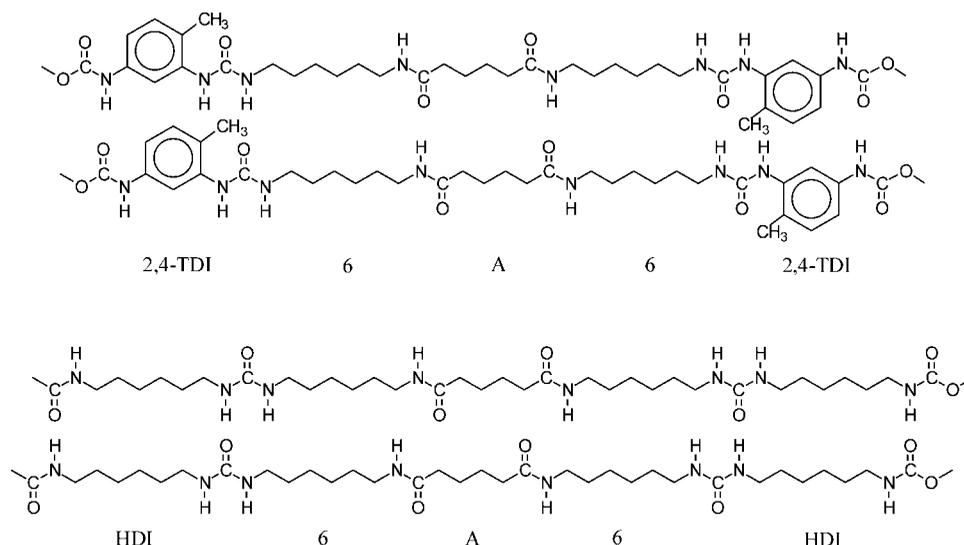


Figure 8 The packing of PEUUA copolymers: 2,4-TDI-6A6-2,4-TDI (top); HDI-6A6-HDI (bottom).

were low, between 0.2 and 0.9%/°C and the melting transition was sharp due to the presence of the monodisperse rigid segments. As the $\Delta G'$ values were low, little early melting was taking place, which indicates that the monodispersity of the rigid segments was maintained during the polymerization and processing of the materials.

The segmented polyurethane based on HDI-PTMO₂₀₀₀-HDI had a storage modulus at 25°C ($G'_{25^\circ\text{C}}$) of 32 MPa, which was a factor two higher than for the polyurethanes based on MDI and 2,4-TDI. The storage modulus at room temperature was dependent on the crystalline content^{5,6,13-15} and the aspect ratio of the crystallites.⁶ The crystalline content depended on the amount of rigid segments and their crystallinities. For HDI-6A6-HDI, the 6A6 crystallinity as determined by FTIR was higher, as was the ΔH_m of this segment. Decreasing the PTMO length to 1270 g mol⁻¹ for the HDI-based polymer did not change the T_g and T_m much but increased the $G'_{25^\circ\text{C}}$. Decreasing the PTMO

length increased the rigid segment content and thereby increased the crystalline content. The loss moduli at room temperature were also low, i.e., 0.5–1 MPa, leading to values for the loss factor $\tan \delta$ below 0.1. Such values suggest a low damping behavior during dynamic loading.

Compression set results

The polymers had CS values varying from 12 to 25% (Table II). The TDI-based polyurethane had a lower compression set compared to the HDI- and MDI-based polyurethanes. The polymer based on HDI displayed a somewhat higher compression set but also a higher rubber modulus than the TDI-based polymer. This behavior was expected, as compression set values are generally lower for polymers with lower moduli. For the same reason, the compression set of the PTMO₁₂₇₀ HDI-based polymer increased with an increasing content of the rigid segment.

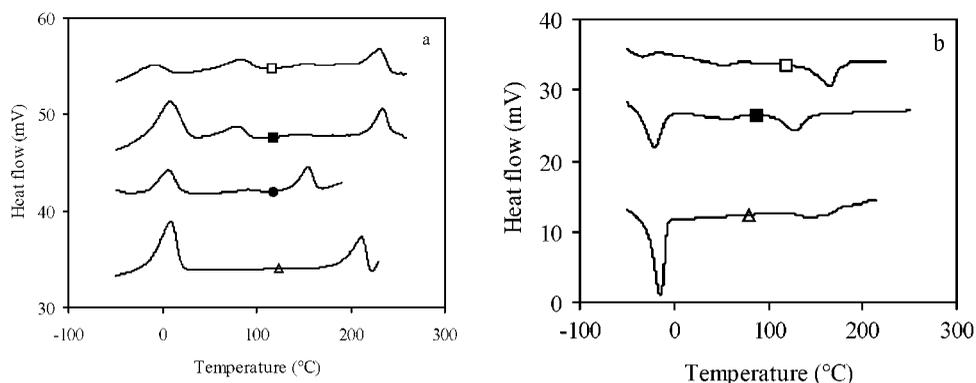


Figure 9 DSC runs displaying (a) heating and (b) cooling of PTMO-based segmented polyurethanes with various isocyanate endcappers: □, PTMO₁₂₇₀-HDI-6A6-HDI; ■, PTMO₂₀₀₀-HDI-6A6-HDI; ▲, PTMO₂₂₀₉-MDI-6A6-MDI; ●, PTMO₁₈₈₆-TDI-6A6-TDI.

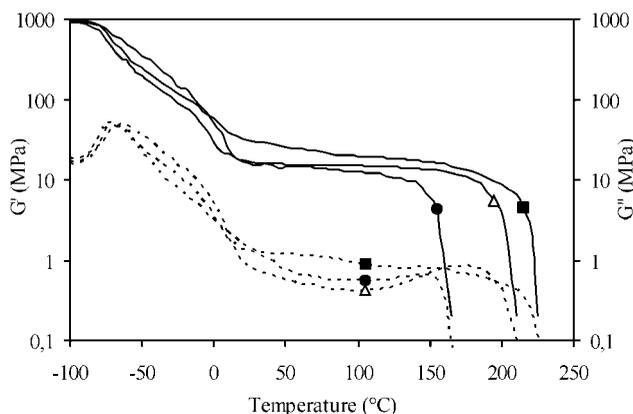


Figure 10 The storage (G') and loss modulus (G'') curves as measured by DMTA for PEUUA: ■, PTMO₂₀₀₀-HDI-6A6-HDI; △, PTMO₂₂₀₉-MDI-6A6-MDI; ●, PTMO₁₈₈₆-TDI-6A6-TDI. The loss moduli are the dotted lines.

Tensile properties

The tensile properties of PEUUA based on the three isocyanate endcappers were studied. Compression molded bars, cut into dumbbells (ISO 37 s2), were used for the tensile tests (Table II). The stress-strain curves correspond to those for thermoplastic elastomer materials. The stress increased linearly with strain at small deformations according to Hooke's Law.²³ The Young's moduli of the MDI- and 2,4-TDI-based polymers were 45 MPa. For the HDI-based polyurethane with equivalent rigid segment content, on the other hand, the Young's modulus was 73 MPa. As expected, these E-moduli were approximately a factor three higher than the storage modulus. The higher value for the HDI copolymers suggest a higher degree of crystallinity and/or a higher aspect ratio of the crystallites as compared to the MDI- and 2,4-TDI-based polyurethanes. The Young's modulus of the HDI copolymer with PTMO₁₂₇₀ was 140 MPa. Thus, by increasing the rigid segment content in the copolymer from 25 to 35 wt %, the modulus was significantly increased. Polyurethanes with concentrations of rigid segment higher than 35 wt % were not studied but it is conceivable that polyurethanes with even higher moduli can be obtained. The yield point was determined by using the Considère construction.²⁴ The yield stress of TPEs increases linearly with crystallinity^{25,26} and the yield stress and yield strain are related to the modulus of a material.²⁷ In general, with increasing modulus, the yield stress increases and the yield strain decreases. Here, the polymer with the highest modulus had the highest yield stress and the lowest yield strain. So far, too few samples have been available to obtain reliable studies on the fracture properties.

The TDI-6A6-TDI copolymer had a lower T_{flex} , a lower compression set and a higher yield strain as compared to the MDI-6A6-MDI copolymer. This sug-

gests that the elastic properties for TDI-6A6-TDI are superior, and since its melting temperature is lower there is a lower risk of degradation during processing. The storage and Young's moduli were similar, as was the yield strength. Thus, with a diamine-diamide extender, TDI polyurethanes gave an interesting combination of properties, however not as good as for the HDI-6A6-HDI copolymers.

Comparison of PEUAs with PEEAs

The properties of the PEUAs (PTMO-DI-6A6-DI) can be compared to those of the PEEAs (PTMO-T6A6T).⁶ The difference in structure between these polymers lies in the fact that the PEUUA have DI-6A6-DI segments with urethane-urea MDI, TDI, or HDI groups instead of T6A6T segments with ester-amide terephthalic groups. The MDI and TDI units are less structural regular than terephthalic groups and may not have cocrystallized fully with the 6A6 units. However, both the PEUAs and PEEAs have a flexible PTMO segment and a 6A6 unit in the monodisperse crystallizable segment.

The amide units in the rigid segments of the PEEAs had a high degree of crystallinity, i.e., ~ 90% (based on DSC and FTIR measurements) as compared with 60% for the MDI- and TDI-based PEUAs and 80% for the HDI-based PEUUA (FTIR measurements) (Table II). The degree of crystallinity for the amide units in the MDI- and TDI-based polymers was lower due to sterical hindrance or an irregular structure of the rigid segments. Upon cooling, the degree of crystallinity of the rigid segments in the PEEAs recovered completely to their initial values,⁶ whereas the crystallinity of the PEUUA only partially recovered. The lower degree of crystallinity and the lower recovery of the crystallinity in the rigid segments of the PEUAs indicate that the crystallization of the rigid segments was not as fast as for the PEEAs with rigid segments of T6A6T. This could also be confirmed by the higher supercooling values of the PEUAs in comparison with those of the PEEAs as determined by DSC measurements.

The storage and E moduli at 25°C for the PEUAs and PEEAs with a PTMO molecular weight of ~ 2000 were comparable, as were those for PTMO 1000. However, the modulus values for HDI-6A6-HDI seem to be a factor 1.5 higher than those with the T6A6T, while the ones based on TDI and MDI displayed somewhat lower values (Table II).

The HDI-6A6-HDI systems thus displayed high modulus values, as a result of the regular hexamethylene group. Surprisingly, the yield strength of the T6A6T system was higher and the compression set lower. It was probable that the amide, urea and urethane groups all took part in the crystallization of HDI-6A6-HDI, whereas in the case of TDI-6A6-TDI

and MDI-6A6-MDI only the amide and urethane groups were involved, and for T6A6T it seemed to be only the amide and no ester groups.^{6,13}

CONCLUSIONS

Polyether(bisurethane-bisurea-bisamide)s (PEUAs) were made from PTMO endcapped with diisocyanate, with a low content of free diisocyanate and uniform 6A6-diamine-diamide extender units. The diisocyanates (DI) used were HDI, MDI, and 2,4-TDI. The resulting polyurethanes were transparent, elastic materials, either colorless or slightly yellow.

The amide units in the rigid segments of the polyurethanes based on HDI, MDI, and TDI were found to be crystalline as determined by FTIR. The crystallinity of the amide units were relatively high (70–80%), but became lower after cooling from the melt (40–60%). IR spectra showed that the polyurethanes based on HDI also had crystalline urea groups. In addition to the crystalline amide parts, the rigid segments based on MDI and TDI also displayed a small amount of crystalline urethane groups.

The melting temperatures of the PTMO₂₀₀₀-DI-6A6-DI were in the range of 165–225°C, and the melting temperatures of the polymers based on HDI (i.e., PTMO_x-HDI-6A6-HDI) were high considering its aliphatic nature, indicating a good packing of the rigid segments. All the PTMO-DI-6A6-DI copolymers had very low T_g values (–72 to –63°C), suggesting that only a very low content of rigid segment was dissolved in the PTMO phase.

The PTMO-DI-6A6-DI polyurethanes had an almost temperature-independent rubber modulus in the plateau region and a sharp melting transition due to the presence of monodisperse rigid segments. This also indicates that during polymerization and processing the monodispersity of the rigid segments was maintained. The copolymers had low compression set values (12–25%).

The Young's and storage moduli were relatively high for the polyurethanes with monodisperse rigid segments. The HDI-based polyurethanes had higher modulus values than the MDI- and 2,4-TDI-based ones. The HDI-based polymer had a rigid segment with a regular hexamethylene structure and no sterical hindrance; thus, resulting in a high degree of crystallinity for the HDI-6A6-HDI segment.

Increasing the concentration of the HDI-6A6-HDI segment in the polymer from 25 to 35 wt % increased the storage modulus from 32 to 50 MPa and the tensile modulus from 72 to 140 MPa. At room temperature, the storage moduli of the polyurethanes with rigid HDI-6A6-HDI segments were superior to those of the T6A6T systems. It is probable that the amide, urea and urethane groups all take part in the crystallization of

the HDI-6A6-HDI. For the TDI-6A6-TDI and MDI-6A6-MDI, on the other hand, only the amide and urethane groups seem to be involved and for the T6A6T polymer, only the amide and none of the ester groups take part.^{6,13}

The TDI-6A6-TDI copolymer had, compared with MDI-6A6-MDI copolymer, slightly better low temperature properties, a lower compression set, a higher yield strain, and a lower melting temperature. The values for modulus and yield strength, on the other hand, were similar between the two materials.

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